

*Supplementary Material for*

Hydrogen-assisted isomerizations of fulvene to benzene  
and of larger cyclic aromatic hydrocarbons

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## Uncertainty in theoretical chemical kinetics

We first consider the high-pressure limit of H + fulvene, where the total rate coefficient is given by the sum of the four rate coefficients for H addition to fulvene. Each of these rate coefficients was obtained via CVT with the methods discussed in Sec. 2 of the main text, where [1]

$$k(T) = \kappa \frac{k_B T}{h} \frac{Q^\ddagger}{Q_R} \exp(-V^\ddagger / k_B T), \quad (\text{S1})$$

$\kappa$  is the tunneling correction,  $Q^\ddagger$  the variationally optimized pseudo-partition function for the transition state,  $Q_R$  is the reactants' partition function, and  $V^\ddagger$  is the variationally optimized zero-point inclusive transition state barrier height. Symmetry numbers and reaction path degeneracies are included in the partition functions, and it is worth noting in the present context that incorrectly assigning symmetry numbers can of course lead to significant errors [2]! Some temperature dependence is not indicated in Eq. (S1), as the variational values of  $Q^\ddagger$  and  $V^\ddagger$  will generally depend on temperature; this dependence was included in the calculations but is neglected in the present discussion of uncertainties. From the point of view of practical applications, it is of interest to consider the effect of uncertainties in  $\kappa$ ,  $Q^\ddagger$ , and  $V^\ddagger$  on the overall uncertainty in the predicted rate coefficient  $k$  as well as the temperature dependence of these uncertainties. The main goal of this discussion is to understand under what conditions the present theoretical predictions (and theoretical kinetics predictions in general) can be expected to achieve kinetic accuracy (defined here as having an uncertainty of less than factor of  $\sim 2$ ).

Equation (S1) is differentiated to give

$$\frac{\sigma_k^2}{k^2} = \frac{\sigma_\kappa^2}{\kappa^2} + \frac{\sigma_{Q^\ddagger/Q_R}^2}{(Q^\ddagger / Q_R)^2} + \frac{\sigma_{V^\ddagger}^2}{(k_B T)^2}, \quad (\text{S2})$$

where we have considered  $\kappa$ ,  $Q^\ddagger/Q_R$ , and  $V^\ddagger$  as independent sources of uncertainty, and  $\sigma_x^2$  is the variance in  $x$ . In what follows, we discuss expected mean unsigned uncertainties of  $\kappa$ ,  $Q^\ddagger$ , and  $V^\ddagger$ , as is typically done when discussing computational results. We then blithely associate the variance with the square of the mean unsigned error.

From Eq. (S2), we immediately note the unavoidable limitation on the accuracy of  $k$  at low temperatures that is associated with uncertainties in  $V^\ddagger$ . At room temperature,  $k_B T = 0.6$  kcal/mol, and so, even neglecting other sources of uncertainty, a value of  $\sigma_{V^\ddagger} < 0.3\text{--}0.6$  kcal/mol is required for kinetic accuracy at 300 K. For systems with more than a few heavy atoms, the high-level theoretical calculations used in practical applications (e.g., QCISD(T)/CBS, CCSD(T)/CBS, etc.) may be expected to have uncertainties of at least  $\sigma_{V^\ddagger} \approx 1$  kcal/mol, principally due to finite basis set and correlation effects. As noted in the main text, the two dual level methods considered for the  $\text{C}_6\text{H}_7$  PES differed in their predictions of the H addition barrier heights by  $\sim 1$  kcal/mol, confirming this conventional uncertainty assignment for this system. Additional uncertainties in  $V^\ddagger$  not tested for here include those in the harmonic zero point energy corrections and those arising from small terms in the Hamiltonian that are typically neglected [3,4], both of which may be as large as several tenths of a kcal/mol. The expected uncertainty in  $V^\ddagger$  is therefore  $\sim 2\text{--}3$  times the uncertainty required to achieve kinetic accuracy at 300 K. The good news for combustion applications is that kinetic accuracy may be achieved above  $\sim 500$  K for  $\sigma_{V^\ddagger} \approx 1$  kcal/mol. We assign  $\sigma_{V^\ddagger} = 1$  kcal/mol in the present analysis. This assignment is likely nearly universal for the quantum chemistry methods used here, although one may assign smaller (or larger) uncertainties if more is known about a particular method's accuracy for a particular class of systems.

The contribution to Eq. (S2) from tunneling is the relative uncertainty in  $\kappa$ . In general, one can identify two sources of uncertainty in any dynamical computation: (1) those present in the computational model, and (2) those arising from the quantum chemical inputs. The well-developed and validated methods of Truhlar notwithstanding, it is nonetheless difficult to quantify the uncertainty associated with the present tunneling models for the large systems studied here. For smaller systems, detailed comparisons with quantum dynamics suggested an inherent "semiclassical" error of only  $\sim 20\%$  for the best tunneling methods [5]. As noted in Sec. 2 of the main text, the Eckart and SCT models differed in their predictions by 20% at 300 K and negligibly so at higher temperatures. The uncertainty arising from

the quantum chemical inputs can be tested numerically, as was done previously for several dual level quantum chemistry methods for the  $\text{H} + \text{HO}_2$  abstraction reaction [6]. Differences of as much as a factor of 4 in  $\kappa$  for the SCT model using different quantum chemical inputs were found at room temperature; the differences were much smaller at higher temperatures where tunneling itself was small. This analysis again suggests that achieving kinetic accuracy at room temperature may be difficult in practical calculations. (This difficulty may be mitigated somewhat by cancellation of the effects of  $\sigma_{V^*}$  and  $\sigma_{\kappa}$  due to correlations in these uncertainties, as noted previously [6].) Again, the situation improves for combustion applications, where the relative uncertainty in  $\kappa$  at elevated temperatures due to the different quantum chemical inputs is small as tunneling is unimportant. In the present analysis we are interested in combustion applications, and so we do not pursue numerical tests of the uncertainty in the tunneling correction for fulvene + H. We instead assume that the dominant source of uncertainty in  $\kappa$  is the choice of the tunneling model, and we assign  $\sigma_{\kappa}$  to be the difference in the SCT and Eckart predictions, which is  $\sim 20\%$  at room temperature and is negligible above 1000 K. For room temperature or atmospheric chemistry applications, more care would be needed quantifying the uncertainty in the tunneling corrections.

Finally, we consider the contribution from  $Q^\ddagger/Q_R$ , which is determined by the vibrational and rotational properties of the transition state and the reactants. Again, we distinguish sources of uncertainty as arising from the choice of the model (which in this case is the rigid rotor/harmonic oscillator or RRHO model) and those arising from the quantum chemical inputs (the calculated rotational constants and frequencies along the minimum energy path). The RRHO model can suffer from significant uncertainties [7], arising principally from anharmonic vibrations such as torsions and coupled low-frequency motions. One-dimensional anharmonic corrections (e.g., for torsions) are often used by us and others to improve the RRHO predictions, although no such corrections were made here. (No obvious torsional corrections were required for the present reactions, as the rings involved prevent large

amplitude torsions. It is, however, reasonable to suspect significant anharmonicity associated with, e.g., H atom bends in aromatic species, as these bends may be better represented by “squarer” wells than the harmonic ones assumed here. Such corrections were not pursued.) The uncertainty in the partition function model is strongly temperature dependent, as both  $Q^\ddagger$  and  $Q_R$  are defined to be one at 0 K, and the RRHO model is exact in this limit. Furthermore, because the vibrational part of  $Q^\ddagger/Q_R$  is the ratio of the product of single-mode partition functions for the transition state and the reactants, one may anticipate significant cancellation in the anharmonicities associated with spectator degrees of freedom. At high temperatures, we estimate that, for the present systems, the uncertainty associated with the neglect of anharmonicity in the RRHO model can be as large as 30%, arising principally from the neglect of anharmonic coupling of the low-frequency interfragment modes at the transition state. (One may expect much larger uncertainties from vibrational anharmonicity for reactions where torsions participate in the reaction [8].) The uncertainty associated with the treatment of the overall rotation and with neglect of the coupling of the rotation to the vibrations in the RRHO model is expected to be small. The uncertainty arising from the computational inputs may be ascertained via numerical tests by comparing predictions of  $Q^\ddagger/Q_R$  using different theoretical methods. This was done in a systematic way for several reactions [6]. Here we simply compare the results of the M06-2X/6-311++G(d,p) method and the CASPT2/aug-cc-pVDZ method with a minimal active space. Frequencies for the reactants and for all but one of the conserved modes were found to be very similar for the two methods. We therefore restrict our error analysis to the three lowest-frequency modes at the saddle points for H addition to fulvene. The CASPT2 method predicts smaller harmonic frequencies than the M06-2X method for these three modes by ~25%, which leads to differences in  $Q^\ddagger/Q_R$  of 30, 40, and 45% at 300, 1000, and 2500 K, respectively. Considering both the model and chemical input sources of uncertainty, we assign  $\sigma_{Q^\ddagger/Q_R} =$  0, 40, 55, 60% at 0, 300, 1000, and 2500 K, respectively. This assignment is likely typical of reactions with loose transition states, low barriers, and no torsions participating in the reaction. Generalizing the

assignment of  $\sigma_{Q^\ddagger/Q_R}$  to other systems is not straightforward. We do note that one may expect significantly more uncertainty in  $\sigma_{Q^\ddagger/Q_R}$  if torsions or other large-amplitude highly-anharmonic motions participate in the reaction.

The three contributions to the uncertainty discussed above and the resulting total uncertainty evaluated using Eq. (S1) is shown in Fig. S4 for a single H-addition rate coefficient. If we consider the uncertainties in the four additions to be independent from one another, the *relative* error in the high-pressure limit rate coefficient decreases by roughly a factor of two. However, it is more likely that the uncertainties are correlated for these similar reactions calculated using the same level of theory, in which case the relative uncertainties in Fig. S4 also represent that of the total high-pressure limit.

Next, we consider the collisionless limit, where, as discussed in the main text, H + benzene is the exclusive product and is formed from three of the adducts only after passing through three additional partially rate limiting saddle points. The uncertainty in the collisionless limit is therefore similar to that of the high-pressure limit, and should be increased somewhat to account for contributions from uncertainties in the kinetics of the later transition states. We do not do so here, and instead assume that this additional uncertainty is small and that the uncertainty is similar for the low- and high-pressure limits. The uncertainty in Fig. S4 is therefore the assigned uncertainty for the total rate coefficient at all pressures.

The uncertainties in Fig. S4 are likely typical of many TST calculations for reactions with a saddle point. If vibrational uncertainties (arising primarily from vibrational anharmonicity) can be mitigated, kinetic accuracy is achievable above ~500 K or so. Predictions at room temperature and colder, on the other hand, require accuracies in threshold energies and tunneling corrections that may not yet be reliably achieved for systems with more than a few heavy atoms. One may be able to assign smaller uncertainties in  $V^\ddagger$  for well-behaved systems and/or for systems with only a few heavy atoms,

where higher-level quantum chemistry calculations are possible; chemical accuracy at room temperature may be within reach for such systems.

Although not directly relevant to the present analysis, it is interesting to consider the uncertainty associated with simpler applications of TST that are often used for the sake of convenience. First, we consider errors associated with the Wigner tunneling correction [9]. For the H addition reactions considered here, Wigner tunneling can be quite accurate, with differences from the SCT and Eckart tunneling corrections of only  $\sim 20\%$ , on average. In fact, the Wigner and Eckart tunneling corrections are very similar for three of the four H-addition reactions, agreeing with each other to better than a few percent; these tunneling corrections themselves are quite small, and are only  $\sim 1.2$  at 300 K. For the H-addition reaction with the largest tunneling correction (the one forming the *tert*-hydrofulvenyl radical), however, Wigner tunneling severely underestimates tunneling at room temperature by almost 40% ( $\kappa_{\text{Wigner}} = 1.8$ ;  $\kappa_{\text{SCT}} = 3.0$ ). This result is in line with past work showing that Wigner tunneling can be accurate but only when tunneling is small. For reactions with significant tunneling corrections (and tunneling corrections may be several orders of magnitude at 300 K), one may expect the uncertainty associated with the Wigner model to be very large. We conclude that Wigner tunneling corrections cannot be reliably used in predictive calculations where tunneling is expected to be important, as the use of Wigner tunneling corrections introduces uncertainties nearly as large as the tunneling correction itself. Second, we consider the uncertainty associated with the neglect of variational effects, which are not always included in TST calculations. As discussed in the main text, variational effects were found to be significant for the H-addition reactions considered here (which have low barriers), reducing the addition rate coefficients by as much as a factor of 2. Furthermore, there is a significant uncertainty associated with the use of Cartesian coordinates to describe the harmonic frequencies away from the saddle points. The use of curvilinear coordinates is available as a standard option in POLYRATE but requires additional user input, which likely discourages their widespread use. We find, however, that the use of Cartesian coordinates introduces an uncertainty of 20% at 300 K, increasing to 60% at 2500 K.

Comparing these values with those in Fig. S4, the uncertainty arising from what some might consider an obscure detail of the calculation can be the dominant source of uncertainty in the calculation at elevated temperature. This effect is likely to be significant only for low-barrier processes, such as the ones considered here. For such cases, we recommend the use of curvilinear coordinates whenever variational effects are significant.

The extent to which correlations in the various sources of uncertainty mitigate the overall uncertainty is difficult to anticipate. Surely there is some cancellation of errors associated with the tunneling correction and the predicted barrier height. It also is reasonable to anticipate correlations that increase the overall error, such as those associated with different quantum chemical methods predicting equilibrium structures with systematically different bond distances. Incorporating these correlations as covariances into Eq. (S1) may have a significant impact on the estimation of the overall uncertainty in theoretical calculations and is beyond the scope of this present analysis.

Note that the master equation generally involves the same quantum chemical inputs and models as Eq. (S1) as well as a collisional energy transfer term. To better understand the uncertainty associated with collisional energy transfer, we consider the simplified case of a unimolecular reaction with one set of products. For such a system, the second-order low-pressure dissociation rate coefficient can be written<sup>10</sup>

$$k_0 = \sum_{J'} \int_0^{E_{J'}} dE' \sum_J \int_{E_J}^{\infty} dE R(E, J; E', J') x(E', J'), \quad (\text{S3})$$

where  $E_J$  is the rotationally adiabatic threshold energy for the total angular momentum  $J$ ,  $E$  is the total energy,  $R$  is the collisional energy transfer term describing the rate of transitions from state  $(E', J')$  to state  $(E, J)$  due to bath gas collisions, and  $x(E, J)$  is the normalized steady state solution of the master equation. The low pressure-limit rate coefficient of a unimolecular reaction is therefore determined by the rate of activating collisions near threshold, and this information is contained in  $R$ ;  $R$  is most often approximated using the so-called single exponential down model where<sup>10</sup>



$$R(E, J; E', J') = Z A \exp(-(E' - E) / \alpha) \varphi \quad \text{for} \quad E < E', \quad (\text{S4})$$

$Z$  is the collision rate (usually assumed to be a Lennard-Jones collision rate),  $A$  normalizes the collision probability,  $\alpha$  is a parameter,  $\varphi$  is a model for  $J$ -dependence that facilitates the solution of the master equation, and the activating wing of  $R$  is determined by enforcing detailed balance. This model requires  $\alpha$ , which is a function of the bath gas and is often written as a function of temperature with two parameters ( $\alpha_{300}$  and  $n$ ),

$$\alpha(T) = \alpha_{300} (T / 300 \text{ K})^n. \quad (\text{S5})$$

One could identify independent sources of uncertainty in Eq. (S3) (e.g.,  $\sigma_a$ ,  $\sigma_z$ , etc...), assign values to these uncertainties based on a critical analysis of both the quantum chemical inputs and models, and differentiate Eq. (S3) to obtain an expression for the total error, as was done above for Eq. (S1). Unfortunately, too little is known about the predictive accuracy of the energy transfer models assumed above to reliably assign uncertainties. In ongoing work, we are performing the kinds of studies required to quantify these uncertainties, but the results we have obtained so far cannot be reliably generalized. We emphasize that in almost every other pressure dependent kinetics calculation involving the solution of a master equation that has appeared in the literature, Eqs. (S3) and (S4) (or very similar equations) were assumed and the values of  $\alpha_{300}$  and  $n$  were either estimated or adjusted to fit the resulting calculated rate coefficient to some experimental values. We and others have previously discussed the shortcomings of the energy transfer models in Eq. (S3) (see Ref. 11 and references therein). As has been widely noted, these models neglect the dependence of energy transfer on the initial rotational state and the initial energy of the target and neglects so-called “supercollisions” that give rise to a “long tail” distribution instead of a single exponential one. The effects of these approximations on the predicted kinetics is largely unquantified. We therefore cannot reliably assign uncertainties based on these studies.

Here we have considered two simple cases where analytic expressions for the rate coefficients may be written, as in Eqs. (S1) and (S3), and analyzed. For more complicated cases, the overall effects of the various sources of uncertainty on the resulting multichannel, multiwell kinetics may be studied using numerical sensitivity analyses. Although not yet routine, methods for performing and interpreting these analyses are actively being developed by several groups. As a very simple example, one can estimate the sensitivity of the predicted branching fractions on our choice of  $\alpha$ . We adjusted  $\alpha$  by a factor of 1.5 and found that the resulting branching fractions shown in Fig. 3 of the main text changed by less than 0.08. Such a numerical sensitivity analysis provides one measure of the uncertainty of the theoretical prediction, but we emphasize that it ignores the uncertainty arising from the choice of the theoretical model for energy transfer. This latter uncertainty may be much larger than the former. More effort is required to understand the reliability of pressure-dependent theoretical kinetics.

In conclusion, one may identify the principal sources of uncertainty in a simple theoretical kinetics calculation for a reaction with a barrier as arising from: the calculated barrier height, the tunneling model, the tunneling quantum chemical inputs, the partition function model, and the partition function quantum chemical inputs. At room temperature and colder, chemical accuracy is difficult to achieve in any calculation with a saddle point as this accuracy requires calculated barrier heights with uncertainties of only few tenths of a kcal/mol (which is not currently feasible for systems with more than a few heavy atoms) as well as very accurate tunneling corrections. At combustion temperatures, however, the uncertainty is determined almost entirely by the uncertainty in the partition functions, suggesting that model development toward more predictive chemical kinetics for combustion should focus on this source of uncertainty. There is significant uncertainty in the models typically used for collisional energy transfer, and more work is required to quantify this uncertainty.

## References

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Figure S4

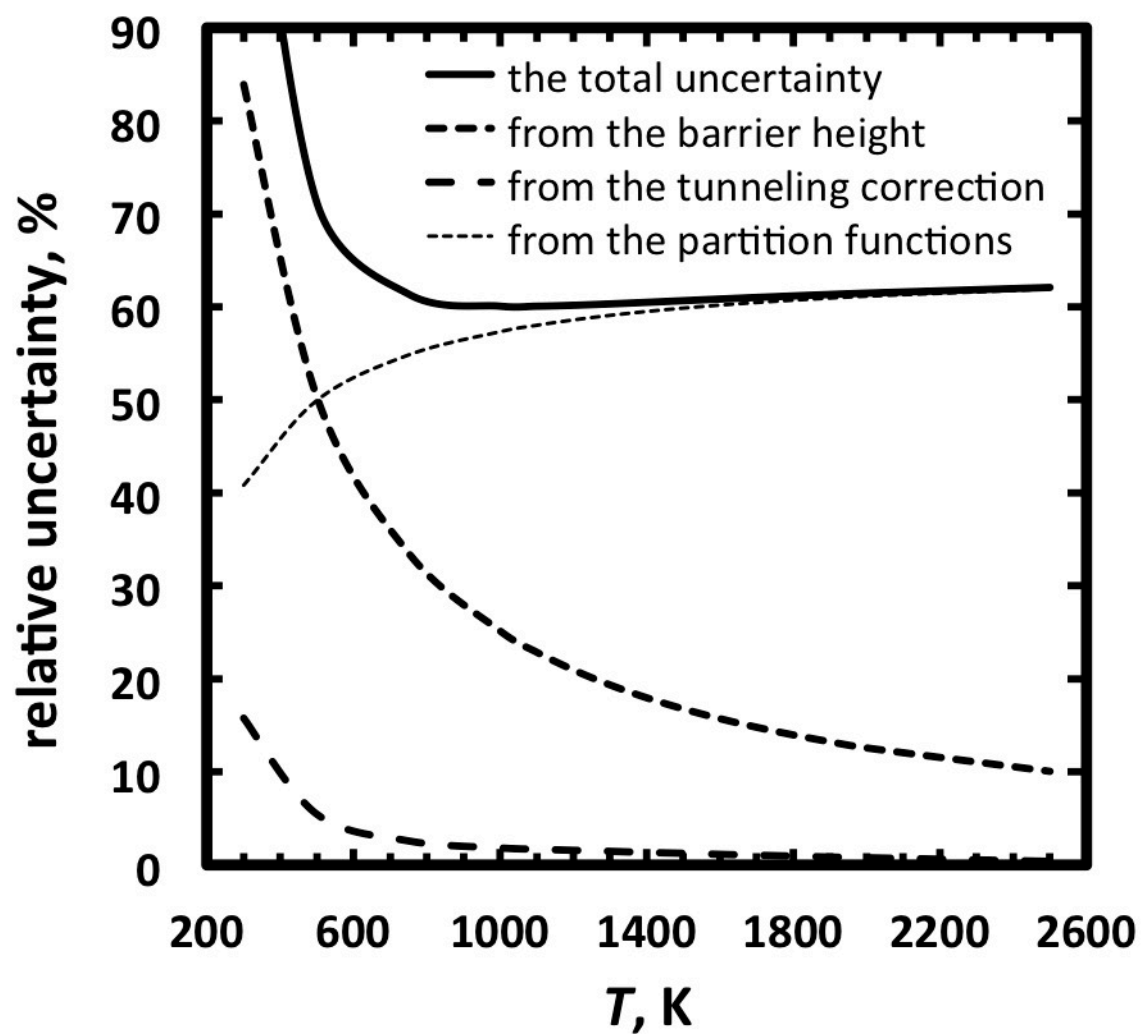


Fig. S4. The relative uncertainty in the theoretical values of  $k$  and the contributions to it arising from uncertainties in the barrier heights, tunneling corrections, and partition functions.